

METHOD OF REMOVING PECVD RESIDUES OF FLUORINATED  
PLASMA USING IN-SITU H<sub>2</sub> PLASMA

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FIELD OF THE INVENTION

The present invention relates to a method of removing  
plasma enhanced chemical vapor deposition (PECVD) residues from  
10 a reaction chamber during a process of forming semiconductors or  
integrated circuits. These residues result from fluorinated  
discharges used to remove unwanted film deposition from PECVD  
chamber walls when preparing semiconductor or integrated  
circuits.

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BACKGROUND OF THE INVENTION

It is known that manufacturing semiconductor devices on a  
wafer entails a number of steps, inclusive of photolithography  
20 and etching, thin film deposition, and the use of ion  
implantation steps alternately performed in order to develop or  
build-up the semiconductor device or wafer. Typically, the  
photolithography steps include coating a wafer with a  
photoresist wherein an ultraviolet photosensitive organic  
25 material is utilized. The photoresist is exposed through a  
mask, after which the resist is developed. Next, the exposed  
photoresist is etched thereby leaving given exposed areas on the  
surface of the wafer. Following the foregoing steps, additional  
processing steps such as deposition, implantation or etching may  
30 be employed on the exposed areas.

In deposition processes, particularly in PECVD processes,  
it is necessary to periodically remove or clean deposition  
material from the chamber or reactor hardware. A fluorine-based

plasma discharge is commonly used to remove dielectric material such as silicon dioxide ( $\text{SiO}_2$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ ), and silicon oxynitrides ( $\text{SiON}$ ). During such fluorinated plasma cleaning,  $\text{AlF}_3$  (which is a by-product of the cleaning) grows on  
5 exposed internal PECVD chamber hardware by reaction of various fluorine species with the aluminum or aluminum based chamber parts. This accumulation of  $\text{AlF}_3$  on the chamber hardware alters the ensuing plasma chemistry and adversely impacts film deposition properties. In essence, the slow accumulation of  $\text{AlF}_3$   
10 causes drifting film properties and process control problems. (Refer to publication by B. Smith, et al, J. Electrochem. Soc. accepted for Nov 2001.)

Eventually, the  $\text{AlF}_3$  must be removed in order to maintain film properties within some process window. Wet chemical  
15 cleaning is commonly used to restore PECVD chamber performance (since  $\text{AlF}_3$  is water soluble). However, wet cleaning unfortunately involves removing the PECVD chamber from operation, disassembling the chamber, and cleaning the chamber parts in a wet chemical bath. This wet chemical cleaning  
20 unfortunately creates considerable chamber downtime during the wet cleaning procedure.

In the past,  $\text{H}_2$  plasma etching of  $\text{AlF}_3$  films on wafers has been demonstrated by S.G. Pearton, et al, Mat.Res.Soc.Symp.Aoc., Volume 282 (1993), p. 131. Pearton et al used  $\text{H}_2$  plasma to  
25 remove  $\text{AlF}_3$  etch-stop layers in GaAs-based wafer processing.

U.S. Patent 5,882,489 disclose processes for cleaning and stripping photoresist from surfaces of semiconductor wafers. The process entails ashing the organic resist from a device, rinsing the device in water, and sputtering the rinsed device to  
30 remove residual contaminants. The stripping step is a dry etching process such as a microwave downstream process, a RIE process, or sequential or simultaneous microwave downstream and

RIE process, wherein the rinsing step is performed with deionized (DI) water, and the sputtering step is performed with argon. The process is especially useful for etching via holes when the holes penetrate a conductive layer and create  
5 insoluble, inorganic contaminants such as  $\text{AlF}_3$ .

A method for etch rate enhancement by background oxygen control in a soft etch system is disclosed in U.S. Patent 6,143,144. This sputter etch cleaning process to remove or sputter off particles from the substrate surface within the  
10 processing chamber is accomplished by:

positioning a first substrate to be processed within a processing chamber, the first substrate including a material layer containing oxygen;

introducing a process gas into the chamber;

15 inductively coupling electrical energy to the process gas in the chamber to form an ionized gas plasma in the chamber;

positioning a second material substrate proximate the first substrate in the processing chamber;

20 biasing the first and second substrates with RF electrical energy so that the plasma etches the first substrate material layer and the second substrate, the material etched from the first substrate material layer producing activated oxygen in the gas plasma;

the second substrate being formed of a material which  
25 reacts with activated oxygen to form a stable oxygen-containing compound such that material etched from the second substrate reduces activated oxygen in the gas plasma;

whereby residual oxygen in the processing chamber is reduced to maintain an etch rate for subsequent sputter etching  
30 processes.

U.S. Patent 5,017,403 disclose the use of plasma-enhanced chemical vapor deposition (PECVD) to form dielectric films. The process entails:

- (a) providing a substrate in a chamber;
- 5 (b) flowing a reactant gas in the chamber;
- (c) generating a plasma between the electrodes by R.F. power to dissociate the gas and deposit a predetermined planarization layer of carbonaceous material on the substrate; while maintaining the
- 10 substrate at a relatively low temperature wherein the layer is soft as deposited and is then hardened by thermal or plasma treatment.

A low pressure and low power  $\text{Cl}_2/\text{HCl}$  process for sub-micron metal etching is disclosed in U.S. Patent 5,976,986. The method

15 entails:

placing aluminum metallization coated on at least one surface with a barrier layer in an etch chamber;

creating a transformer coupled plasma from  $\text{Cl}_2$ ,  $\text{HCl}$ , and an inert gas within the etch chamber, without a magnetic field,

20 using separately powered electrodes positioned above and below aluminum metallizations wherein each of the electrodes are powered by less than 350 Watts, and wherein the pressure in the etch chamber is less than 15 milliTorr;

etching the aluminum metallizations with ions and radicals

25 formed in the plasma; and adjusting a concentration of the  $\text{Cl}_2$  in the plasma during the creating and etching steps between a first higher concentration during etching of the aluminum metallization and a second lower concentration during etching of the barrier layer.

30 The addition of hydrogen to plasma is used to reduce corrosion during the etching of aluminum layers.

In the art of PECVD processing where fluorinated plasma discharges are utilized, there is a need to remove unwanted residues from PECVD chamber hardware without wet cleaning the chamber (i.e., disassembling the chamber and cleaning the chamber parts in a wet chemical bath), which results in considerable chamber downtime.

#### SUMMARY OF THE INVENTION

One object of the present invention is to provide an improved method for removing PECVD chamber residues resulting from fluorinated plasma cleaning during a process for forming semiconductors or integrated circuits.

Another object of the present invention is to provide a method for removing PECVD chamber residues of  $\text{AlF}_3$  or derivatives thereof that alter plasma chemistry and adversely impacts film deposition properties.

A further object of the present invention is to provide a method for removing PECVD chamber residues resulting from fluorinated plasma cleaning; namely,  $\text{AlF}_3$  or its derivatives, by utilizing in-situ  $\text{H}_2$  plasma or mixtures containing  $\text{H}_2$ , and thereby avoiding wet chemical cleaning which requires disassembling the chamber, cleaning the chamber parts in wet chemical baths, and incurring considerable chamber downtime during the wet chemical cleaning procedure.

A further object yet still of the present invention is to provide a method for removing PECVD chamber residues resulting from fluorinated plasma cleaning by using in-situ  $\text{H}_2$  plasma to restore chamber performance without opening the chamber, and thereby increasing tool availability and freeing maintenance resources.

In general, the invention process of using  $\text{H}_2$  plasma to etch  $\text{AlF}_3$  accumulated in the reaction chamber and to improve control

over film properties is accomplished after a fluorinated plasma clean by:

subjecting the reaction chamber to a mixture of He/H<sub>2</sub> at a flow rate of 1,000/200sccm (standard cubic centimeters per minute), at about 750W rf, at about 0.8Torr for about 5 seconds to strike the plasma, and then cleaning the chamber by subjecting it to H<sub>2</sub> at about 500sccm for 5-60 seconds, at about 500W rf, at about 0.5Torr.

#### 10 BRIEF DESCRIPTION OF THE DRAWING FIGURES

FIG. 1 is a graph showing film thickness U% versus number of wafers processed, and reflects drifting film properties in a PECVD chamber between wet cleans (denoted WC).

15 FIG. 2 depicts a reaction chamber after one or more fluorinated plasma cleans and shows AlF<sub>3</sub> build-up on the powered electrode.

FIG. 3A is a graph generally showing SiON film thickness versus rf power (DARC is a specific SiON application), consistent with the accumulation of AlF<sub>3</sub> on a shower head to affect power coupling into plasma.

FIG. 3B is a graph generally depicting SiON optical constants refractive index (n) and extinction coefficient (k) versus rf power, which is the primary knob for adjusting plasma density. The changes that are induced by reducing power are consistent with the film drift problem.

FIG. 4A is a graph depicting change in SiON film thickness by location across a wafer after processing several thousand wafers and represents the impact of non-uniform AlF<sub>3</sub> build-up (concentrated in center), and provides some indication as to why the U% drifts.

FIG. 4B is a graph showing the change in optical properties,  $n$  and  $k$ , by location across a wafer after processing several thousand wafers due to non-uniform  $\text{AlF}_3$  build-up (concentrated in the center), where there is diminished plasma density in the center of the chamber.

FIG. 5A is a graph comparing the number of wafers processed between wet cleans (performed as necessary to control  $\text{SiON}$  film thickness  $U\%$ ) for processes with and without in-situ  $\text{H}_2$  plasma.

FIG. 5B is a graph showing drift in  $\text{SiON}$  thickness  $U\%$ . The rate of drift is greatly reduced after introducing  $\text{H}_2$  plasma to remove  $\text{AlF}_3$  residues.

FIG. 6 is a graph generally showing the influence of rf power on H-atom concentration in a plasma as predicted by actinometry for a mixture of 99%  $\text{H}_2$  and 1% Ar.

FIG. 7 is a graph generally showing the effect of pressure on H-atom concentration in a plasma as predicted by actinometry for a mixture of 99%  $\text{H}_2$  and 1% Ar.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENT OF INVENTION

In PECVD processing, a fluorine containing discharge (here as a mixture of  $\text{CF}_4 + \text{N}_2\text{O}$ ) is introduced periodically into the chamber to remove excess deposition material (e.g.,  $\text{SiO}_2$  or  $\text{Si}_3\text{N}_4$ ) in order to maintain consistent film properties from wafer to wafer. The fluorinated discharge leaves a light residue in the chamber that accumulates over successive treatments. The build-up in the chamber was identified as  $\text{AlF}_x$  by EDX (energy dispersive x-ray analysis).

Accumulation of fluorine discharge residue gradually affects film deposition properties. An example of said drifting film properties in a PECVD chamber is shown in the graph of FIG.

1 which shows SiON film thickness uniformity (U%) versus the  
number of wafers processed. In general, all film properties  
including film thickness, thickness U%, n, k, and stress are  
subject to gradual drift depending on the sensitivity of the  
5 particular process and process parameter. Wet cleans (denoted WC  
in FIG. 1) are invasive procedures typically used to remove  
chamber residue and restore film properties. After the wet  
clean (WC), the SiON film thickness profile is relatively flat.  
With use, the profile becomes center thin and U% increases. U%  
10 is governed by the formula:

$$U\% = 100 \cdot \frac{s}{\bar{x}}$$

where s is the standard deviation of film thickness measured at  
nine sites on a wafer and  $\bar{x}$  is the mean of the film thickness  
measured at the same nine sites.

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The build-up of  $AlF_3$  on the powered electrode (typically the  
showerhead in commercial reactors) may be seen in the parallel  
plate plasma reactor diagram of FIG. 2. The  $AlF_3$  is a dielectric  
that inhibits the coupling of rf power into the plasma,  
20 resulting in reduced plasma density. An evenly distributed  $AlF_3$   
build-up affects the plasma chemistry which ultimately  
determines the properties of the film deposited. FIG. 3A and 3B  
show the impact of plasma density on film properties as rf power  
directly modulates plasma density (i.e., higher rf power implies  
25 higher plasma density). Because the transfer of energy is  
affected uniformly across the chamber, film properties are  
impacted in a roughly uniform manner.

In practice the fluorinated discharge that produces the  $AlF_3$   
residue may not be perfectly uniform. An uneven distribution of  
30  $AlF_3$  (or other derivatives from fluorinated plasma cleaning) on  
the showerhead causes an uneven transfer of power into the



plasma, thereby leading to uneven plasma density across the chamber. Since plasma density plays a prominent role in the reaction chemistry, varying the plasma density locally can yield locally different film properties, as may be seen from FIGS. 4A and 4B, which shows respectively, a change in thickness versus location on a wafer and a change in  $n$  and  $k$  versus location on a wafer during the  $\text{AlF}_3$  build-up. In FIG. 4A, the thickness versus position represents film properties over several thousand wafers due to non-uniform  $\text{AlF}_3$  build-up (concentrated in the center), and thereby provides some indication as to why the  $U\%$  drifts. In FIG. 4B, there is also shown the change in  $n$  and  $k$  versus position over several thousand wafers due to non-uniform  $\text{AlF}_3$  build-up (concentrated in the center) where there is diminished plasma density in the center of the chamber.

This phenomenon is the same for oxide and nitride films, but to a slightly lesser degree.

Wet cleaning PECVD chambers is typically performed to remove  $\text{AlF}_3$  residue and restore (i.e., control) film properties. Wet cleans temporarily remove a chamber from operation and require maintenance resources for disassembling the chamber, initiating the wet chemical clean, and eventually reassembling the chamber. In large scale semiconductor manufacturing where a large number of PECVD chambers are employed, frequent chamber wet cleans can easily impact overall manufacturing productivity by reducing chamber availability and consuming maintenance resources. The invention process uses in-situ  $\text{H}_2$  plasma to reduce or remove fluorinated discharge residues, namely  $\text{AlF}_3$ , in a less invasive manner. In essence, the invention process of removing this build-up from fluorinated plasma cleaning by using in-situ  $\text{H}_2$  plasma eliminates or reduces the need for wet chemical cleaning, thereby improving chamber availability and freeing maintenance resources. The improvement realized by employing

in-situ  $H_2$  plasma is illustrated in FIG. 5A which compares the number of wafers processed between SiON thickness U% failures with and without  $H_2$  plasma cleaning. FIG. 5B shows SiON thickness U% over time and reflects a significant reduction in U% drift rate after beginning  $H_2$  plasma treatments. The invention process is the first to utilize  $H_2$  plasma etching of  $AlF_3$  to control chamber conditions in order to enhance control over PECVD processes and the properties of the deposited film. The invention process is the first in-situ chemical process for removal of fluorinated discharge residues. As such, the  $H_2$  plasma process has distinct advantages over the wet clean process typically used in terms of chamber productivity and use of maintenance resources.

While the preferred embodiment of the invention applies the  $H_2$  plasma cleaning in-situ, it should be noted that an ex-situ process would also suffice.

Hydrogen atoms generated in  $H_2$  plasma are responsible for removal of  $AlF_3$  by reduction reaction. Consequently, it is desirable to maximize the H-atom concentration (denoted [H]) for efficient removal of  $AlF_3$  residues. From FIG. 6, it can be seen that the high rf power is conducive to high hydrogen atom concentration. The use of optical emission spectroscopy (OES) and actinometry, a related technique, is utilized to identify process conditions that maximize H-atom concentration in the plasma based on the relative emission from excited H and Ar atoms.

Referring to FIG. 7, it may also be seen that low pressure is also conducive to high [H]. Therefore, it is clear from FIGS. 6 and 7 that the combination of low pressure and high power are together conducive to high [H]. In general, the H-

atom concentration in the plasma may be determined by the following formula:

$$\frac{\text{Intensity of H}}{\text{Intensity of Ar}} \cdot \alpha [\text{H atom}]$$

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By use of H<sub>2</sub> plasma to etch AlF<sub>3</sub> on the faceplate of the chamber, improved control over film properties was obtained. This in-situ procedure effectively eliminates the need for wet cleans and increases tool availability. Restoration of chamber performance by removing AlF<sub>3</sub> removes AlF<sub>3</sub> growth on the chamber wall that alters PECVD chamber performance, and the invention process for removing the AlF<sub>3</sub> is superior to removal by wet chemical or mechanical means, as these means require considerable chamber downtime. Further, the in-situ H<sub>2</sub> plasma removes AlF<sub>3</sub> without opening the chamber, thereby increasing tool availability and freeing maintenance resources.

While the invention has been described in terms of its preferred embodiments, those skilled in the art will appreciate that the invention may be practiced with modifications within the spirit and scope of the appended claims.

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